Synthesis of organically templated nanoporous tin (II/IV) phosphate for radionuclide and metal sequestration

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Nanoporous tin (II/IV) phosphate materials, with spherical morphology, have been synthesized using cetyltrimethylammonium chloride ($CH_3(CH_2)_{16}N(CH_3)_3Cl$) as the surfactant. The structure of the material is stable at 500°C; however, partial oxidation of the material occurs with redox conversion of Sn^{2+} to Sn^{4+}, resulting in a mixed Sn(II)/ Sn(IV) material.

Nanoporous materials offer an efficient way of selectively sequestering many types of metals and radionuclides in a very small volume. The high surface area of a nanoporous structure enhances mass transfer in sequestration applications and enables ions to be highly concentrated in a very small volume of material. Operations related to nuclear energy and weapons production have produced significant quatnities of radioactive waste over the last half century. The waste is targeted to be processed and buried in a deep geological repository (e.g. Yucca Mountain, Nevada). The current proposal is to include "getter materials" with this waste in order to sequester any radionuclides that might leach from the wasteforms. Of particular interest in this regard are the long-lived actinide species (e.g. Pu, Am, Np, etc.) and the anions (e.g. pertechnetate, iodide, etc.). Getter materials must be able to survive long-term exposure to elevated temperatures (>150°C) and moderately high radiation fluxes. The frailty of organic components towards radiolytic degradation precludes their use for either structure or function in the final getter material.

Over the last decade, metal phosphates have been extensively studied due to their potential use in catalysis, ion-exchange, and phase separation[1,2]. Since the first open-framework tin phosphates were prepared nearly 15 years ago, there has been interest in the structural flexibility of tin phosphates crystallizing in one-dimensional, three-dimensional, or layered structures[3-12]. Open-framework tin phosphates have been prepared by direct precipitation[10] and by incorporating organic amines into the crystal lattice[3-9,11,12]. Surfactant-templated, open-framework tin phosphates have been reported using structure directing amine compounds including ethylenediamine[4,7,12], 1,6-diaminohexane[5], 1,2-diaminopropane[6], 1,8-diaminooctane[5], and 1,4-diaminobutane[6]. Only recently, however, has a nanoporous tin (IV) phosphate been reported, and, to date, this is the only known report of a nanoporous tin phosphate[13]. The cationic quaternary ammonium salt $CH_3(CH_2)_{14}N(CH_3)_3Br$ was used as the surfactant. The use of CTAB as surfactant resulted in surface areas of 230 m^2/g, and pore sizes of 35-38 Å. Although the pore size was reduced from 39 to 35 Å, the structure was stable following calcination.

The goal of this study was to produce a similarly stable, mesoporous solid using tin (II) as the starting material to produce a material capable of sequestering redox sensitive species such as pertechnetate, neptunium, chromium, iodide, etc. The large pores afforded with quaternary ammonium surfactants and the high surface area of a nanoporous structure are valuable features for enhanced mass transfer in sequestration applications. This communication summarizes efforts to make a nanoporous tin(II) phosphate phase.

The synthesis method consists of preparing 200 mL of 6.87 mmol CTAC, $CH_3(CH_2)_{14}N(CH_3)_3Cl$, in deionized water. The solution is acidified with 0.626 mL of concentrated phosphoric acid. A concentrated solution of 15.222 g stannous chloride was dissolved in 100 mL hydrochloric acid. 2.5 mL of $SnCl_2$/HCl solution was added with stirring at room temperature to the acidified surfactant. The solution stirred for 30 minutes at room temperature and was place in an oven at 65°C for 48 – 72 hours. The synthetic material was collected via vacuum filtration using a 0.45μm filter, washed with deionized water and dried under ambient conditions. Chemical analysis of the synthetic material indicates the structure is composed of Sn:P:O with a ratio of 1:1:5.

Calcination of the as-synthesized material at 500°C produced a material with a surface area of 262 m^2/g. The XRD pattern of the surfactant-$SnPO_4$ and calcined $SnPO_4$ are shown in Fig. 1. The *d* spacing of the 100 plane in surfactant-$SnPO_4$ is 5.01 nm, whereas after calcintation it was reduced to 4.62 nm. Subjecting the nanoporous $SnPO_4$ (NP-SnPO) to high temperatures during calcination seem to have little impact on pore size.

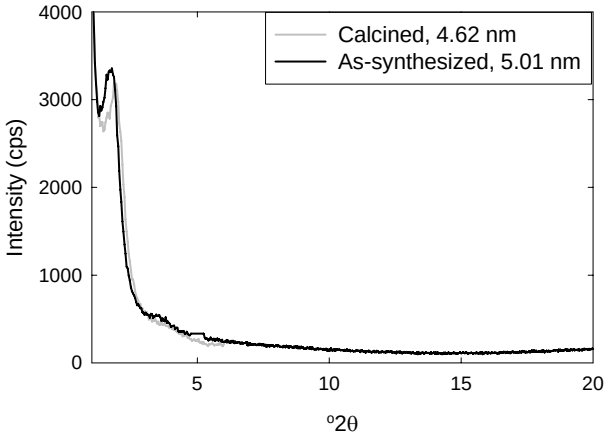

Figure 1. X-ray diffraction pattern for surfactant-$SnPO_4$ and calcined SnPO4.

Selected-area electron diffraction analysis of a typical tin phosphate (NP-SNPO1) illustrates a completely amorphous structure (Figure 2a). Analyses with high-resolution transmission-electron microscopy (HR-TEM) revealed a spherical particle morphology approximately 150 nm across, with uniform pore distribution narrowly distributed around 2 nm (Figure 2b). It was also observed that directly precipitated NP-

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See http://www.rsc.org/suppdata/cc/b0/b000000a/

SNPO materials, in addition to being thermally stable (500°C), are chemically stable over the entire pH range (pH = 0 to 14).

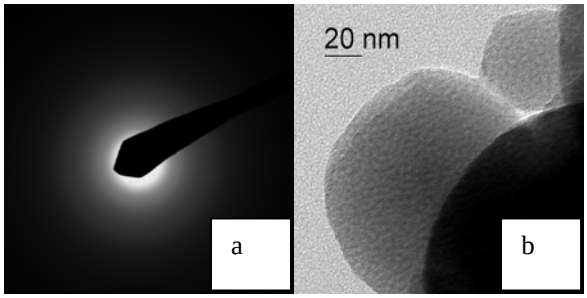

Figure 2. (a) Selected-area electron diffraction pattern indicating amorphous structure. (b) Nanoporous tin (II) phosphate with uniform pore distribution narrowly distributed around 2 nm.

Preliminary batch contact studies have been conducted to assess the effectivness of NP-SnPO in sequestering redox sensitive metals and radionuclides, technetium(VII), neptunium(V), thorium(IV), and a toxic metal, chromium(VI), from aqueous matrices (Table 1). Equilibrium was achieved in less than an hour at a solution to solids ratio of 100, therefore a batch contact time of 2 hours was used to insure that these values represent true equilibrium conditions. Under these conditions the nanoporous, calcined tin (II) phosphate removed > 95% of all contaminants investigated from solution. Distribution coefficients, K_d, are defined as a mass-weighted partition coefficient. K_d values were typically > 10,000 in groundwater. At a solution to solids ratio of 100, a K_d value of 10,000 indicates that at equilibrium there was 100 times as much contaminant in the nanoporous metal phosphate phase as there was remaining in the supernantant solution.

Table 1. Affinity of NP-SnPO for Tc(VII), Np(V), Th(IV), and Cr (VI)

Sorbate	Test Matrix	K_d (mL/g)
Tc(VII)	0.002 M $NaHCO_3$	> 9.0×10^4
Np(V)	0.002 M $NaHCO_3$	> 1.1×10^5
Th(IV)	DI Water	> 2.2×10^4
Cr(VI)	0.002 M $NaHCO_3$	> 5.6×10^4
Cr(VI)	GW + 0.02 M Na_2SO_4	> 4.4×10^4

Data obtained via X-Ray Absorption Near Edge Spectra/Extended X-Ray Absorption Fine Structure (XANES/EXAFS) clearly illustrate the sequestration of Tc(VII), Np(V), and Cr(VI) with NP-SNPO occurs through redox-coupled reactions with the target metals being reduced to their least soluble valence states, namely, Tc(IV), Np(IV), and Cr (III), with oxidation of Sn in NP-SnPO (Figure 3). Although lacking spectroscopic data, we surmise that Th(IV) adsorption on NP-SnPO is due to Lewis acid-base interaction with PO_4 groups.

These nanoporous tin (II) phosphates exhibited significant promise as sorbent materials for anionic and redox sensitive metals and actinides. The detailed kinetic studies of these materials will be published in due course.

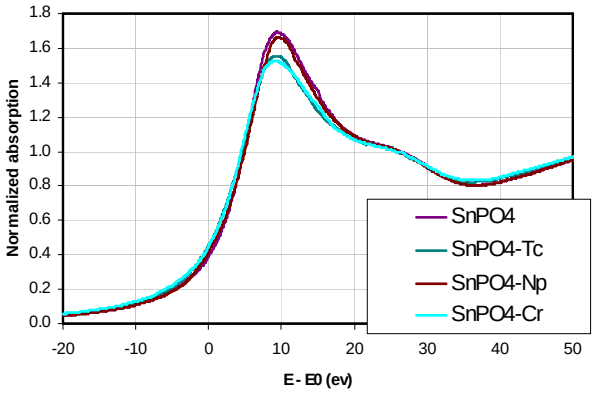

Figure 3. EXAFS spectra of NP-SnPO collected after batch sequestration tests with Tc(VII), Np(V), and Cr(VI). Data clearly illustrateate the oxidation of NP-SNPO with concurrent reduction of the target metal contaminant.

Notes

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